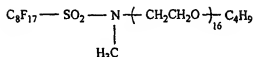
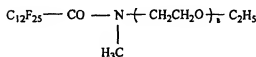
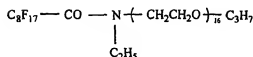


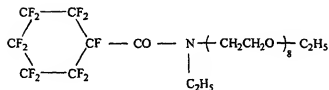
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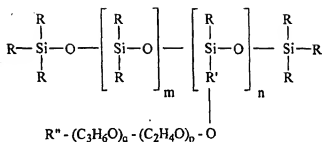
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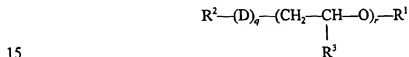


Suitable nonionic surfactants incorporating a polyalkylene oxide moiety
 and an insoluble polysiloxane moiety (nonionic polysiloxane surfactant) may
 comprise compounds in which the polysiloxane moiety has a linear, polysiloxane
 backbone having polyalkylene oxide units (such as the -R³O- units defined above)
 pendant from the polysiloxane backbone. The polyalkylene oxide units are
 preferably linked to the polysiloxane through ether linkages. The polyalkylene
 oxide moiety of the nonionic polysiloxane surfactant may also have the structure -
 R³O- as defined above. Examples of such nonionic polysiloxane surfactants may
 be represented by the following formula:

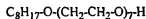
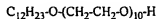


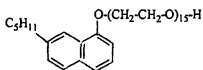
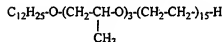
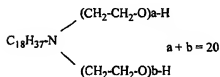
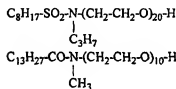
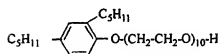
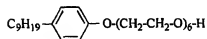
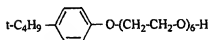
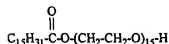
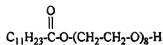
wherein each R is independently a lower alkyl having from 1 to 4 carbon atoms, R' is a lower alkylene moiety having from 1 to 4 carbon atoms, R'' is hydrogen or a lower alkyl moiety of from 1 to 4 carbon atoms, m is an integer from 5 to 100, n is an integer from 2 to 50, p is an integer from 5 to 50, and q is an integer from 0 to 50. Compounds of this class are sold by Union Carbide Co., under the trade name of SILWET, and include SILWET L-7605, SILWET L-77, SILWET L-7001, and the like.

10 Another class of suitable non-ionic polyoxyethylene surfactants of the present invention can be represented by the following formula:



wherein R² represents an alkyl group having 1 to 30 carbon atoms, an alkenyl group having 1 to 30 carbon atoms, or an aryl group having 6 to 30 ring atoms (such as phenyl or naphthyl) or a combination thereof, R¹ and R³ each independently represent a hydrogen atom or a methyl group, D represents a divalent group such as —O—, —S—, —COO—, —NR₄—, —CO—NR₄—, or —SO₂—NR₄—, wherein each R₄ may independently represent a hydrogen atom or an alkyl group having 1 to 12 carbon atoms, q represents 0 or 1 and r represents an integer of 2 to 50. Examples of non-ionic polyoxyalkylene surfactants according to this formula are illustrated below.





In addition to the curable binder component, the surface treated inorganic oxide particles, the antistatic agent, and the nonionic surfactant, the ceramer composition may further include a solvent and other optional additives. For example, if desired, the composition may include a solvent to reduce the viscosity of the composition in order to enhance the coating characteristics. The appropriate viscosity level depends upon various factors such as the coating thickness,

application technique, and the type of substrate material onto which the composition is applied. In general, the viscosity of the coating precursor composition at 25°C is about 1-200 centipoise, preferably about 3-75 centipoise, more preferably about 4-50 centipoise, and most preferably about 5-20 centipoise when measured using a Brookfield viscometer with a No. 2 cv spindle at a spindle speed of 20 rpm. In general, sufficient solvent is used such that the solids content of the composition is about 5-99%, preferably about 10-70%, more preferably about 15-50%, and most preferably about 30% by weight solids.

The solvent is selected to be compatible with the other components included in the composition. As used in this context, "compatible" means that there is minimal phase separation between the solvent and the other components. Additionally, the solvent should be selected such that the solvent does not adversely affect the curing properties of the composition or attack the material of the substrate. Furthermore, the solvent should be selected such that it has an appropriate drying rate. That is, the solvent should not dry too slowly, which would slow down the process of making a coated substrate. It should also not dry too quickly, which could cause defects such as pin holes or craters in the resultant coating. The solvent can be an organic solvent, water, or combinations thereof. Representative examples of suitable solvents include lower alcohols such as ethanol, methanol, isopropyl alcohol, and n-butanol; ketones such as methyl ethyl ketone and methyl isobutyl ketone; glycols; glycol ethers; combinations thereof, and the like. Most preferably, the solvent is isopropanol. Using the procedure described below for making a ceramer composition, the solvent may also include a small amount, e.g., about 2% by weight, of water.

The ceramer compositions of the present invention also may include a leveling agent to improve the flow or wetting of the composition on the substrate. If the composition does not properly wet the substrate, this can lead to visual imperfections (e.g., pin holes and/or ridges) in the coating. Examples of leveling agents include, but are not limited to, alkylene oxide terminated polysiloxanes such as that available under the trade designation "DOW 57" (a mixture of dimethyl-, methyl-, and (polyethylene oxide acetate-capped) siloxane) from Dow Corning,

Midland, MI, and fluorochemical surfactants such as those available under the trade designations FC430, FC431, and FX313 from 3M, St. Paul, MN. The coating precursor composition can include an amount of a leveling agent effective to impart the desired result. Preferably, the leveling agent is present in an amount
5 up to about 3% by weight, and more preferably about 0.5-1%, based on the total weight of the composition solids. It should be understood that combinations of different leveling agents can be used if desired.

During the manufacture of an abrasion resistant coating of the type including a free radically curable binder component, the coated composition
10 preferably is exposed to an energy source, e.g., heat or radiation, that initiates the curing process of the ceramer coating. This curing process typically occurs via a free radical mechanism, which can require the use of a free radical initiator (simply referred to herein as an initiator, e.g., a photoinitiator or a thermal initiator) depending upon the energy source used. If the energy source is an electron beam,
15 the electron beam generates free radicals and no initiator is typically required. If the energy source is heat, ultraviolet light, or visible light, an initiator is often required. When the initiator is exposed to one of these energy sources, the initiator generates free radicals, which then initiates the polymerization and crosslinking.

Examples of suitable free radical thermal initiators include, but are not
20 limited to, peroxides such as benzoyl peroxide, azo compounds, benzophenones, and quinones. Examples of photoinitiators that generate a free radical source when exposed to visible light radiation include, but are not limited to, camphorquinones/alkyl amino benzoate mixtures. Examples of photoinitiators that generate a free radical source when exposed to ultraviolet light include, but are not
25 limited to, organic peroxides, azo compounds, quinones, benzophenones, nitroso compounds, acryl halides, hydrozones, mercapto compounds, pyrylium compounds, triacrylimidazoles, bisimidazoles, chloroalkyltriazines, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ethers and methylbenzoin, diketones such as benzil and diacetyl, phenones
30 such as acetophenone, 2,2,2-tri-bromo-1-phenylethanone, 2,2-diethoxyacetophenone, 2,2-dimethoxy-2-phenylacetophenone, 2,2,2-tribromo-1(2-

nitrophenyl)ethanone, benzophenone, 4,4-bis(dimethylamino)benzophenone, and acyl phosphates. Examples of commercially available ultraviolet photoinitiators include those available under the trade designations "IRGACURE 184" (1-hydroxycyclohexyl phenyl ketone), "IRGACURE 361" and "DAROCUR 1173"

5 (2-hydroxy-2-methyl-1-phenyl-propan-1-one) from Ciba-Geigy. Typically, if used, an amount of an initiator is included in the ceramer composition to effect the desired level and rate of cure. Preferably, the initiator is used in an amount of about 0.1-10%, and more preferably about 2-4% by weight, based on the total weight of the ceramer composition without solvent. It should be understood that

10 combinations of different initiators can be used if desired.

In addition to the initiator, the ceramer composition of the present invention can include a photosensitizer. The photosensitizer aids in the formation of free radicals that initiate curing of the prepolymers, especially in an air atmosphere. Suitable photosensitizers include, but are not limited to, aromatic ketones and

15 tertiary amines. Suitable aromatic ketones include, but are not limited to, benzophenone, acetophenone, benzil, benzaldehyde, and o-chlorobenzaldehyde, xanthone, tioxanthone, 9,10-anthraquinone, and many other aromatic ketones. Suitable tertiary amines include, but are not limited to, methyldiethanolamine, ethyldiethanolamine, triethanolamine, phenylmethyl-ethanolamine,

20 dimethylaminoethylbenzoate, and the like. Typically, if used, an amount of initiator is included in the precursor compositions to effect the desired level and rate of cure. Preferably, the amount of photosensitizer used in the compositions of the present invention is about 0.01-10%, more preferably about 0.05-5%, and most preferably about 0.25-3% by weight, based on the total weight of the ceramer

25 composition without solvent. It should be understood that combinations of different photosensitizers can be used if desired.

Polymeric materials are known to degrade by a variety of mechanisms. Common additives that can offset this are known as stabilizers, absorbers, antioxidants, and the like. The compositions of the present invention can include

30 one or more of the following: ultraviolet stabilizer, ultraviolet absorber, ozone stabilizer, and thermal stabilizer/antioxidant.

An ultraviolet stabilizer and/or ultraviolet absorber improves weatherability and reduces the "yellowing" of the abrasion resistant coating with time. An example of an ultraviolet stabilizer includes that available under the trade designation "TINUVIN 292" (bis(1,2,2,6,6-pentamethyl-4-piperidiny)sebacate) and an example of an ultraviolet absorber includes that available under the trade designation "TINUVIN 1130" (hydroxyphenyl benzotriazole), both of which are available from Ciba-Geigy. The composition can include an amount of either an ultraviolet stabilizer and/or an ultraviolet absorber to impart the desired result. Preferably, the ultraviolet stabilizer or absorber is present in an amount up to about 10% by weight, and more preferably about 1-5%, based on the total weight of the ceramer composition without solvent. It should be understood that combinations of different ultraviolet stabilizers and absorbers can be used if desired.

An ozone stabilizer protects against degradation resulting from reaction with ozone. Examples of ozone stabilizers include, but are not limited to, hindered amines such as that available under the trade designation "IRGONOX 1010" available from Ciba-Geigy and phenoltriazine commercially available from Aldrich. The ceramer composition can include an amount of an ozone stabilizer to impart the desired result. Preferably, the ozone stabilizer is present in an amount up to about 1% by weight, more preferably about 0.1-1.0%, and most preferably about 0.3-0.5%, based on the total weight of the ceramer composition without solvent. It should be understood that combinations of different ozone stabilizers can be used if desired.

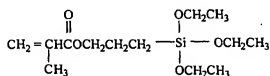
A thermal stabilizer/antioxidant reduces the amount of yellowing as a result of weathering. Examples of such materials include, but are not limited to, low melting hindered phenols and triesters. Specific examples include 2,6-di-tert-butyl-4-methylphenol commercially available under the trade designation "ULTRANOX 226" antioxidant from Borg Warner Chemicals, Inc., Parkersburg, NY; octadecyl 3,5-di-tert-butyl-4-hydroxyhydroxycinnamate commercially available under the trade designations "ISONOX 132" antioxidant (Schenectady Chemicals, Inc., Schenectady, NY) or "VANOX 1320" antioxidant (Vanderbilt Co., Inc., Norwalk, CT). The coating precursor composition can include an

amount of the thermal stabilizer/antioxidant to impart the desired result. Preferably, the thermal stabilizer/antioxidant is present in an amount up to about 3% by weight, and more preferably about 0.5-1%, based on the total weight of the coating precursor composition without solvent. It should be understood that

- 5 combinations of different thermal stabilizers/antioxidants can be used if desired.

According to one approach for making an antistatic, coatable, ceramer composition of the present invention, an aqueous sol of colloidal inorganic oxide particles e.g., silica, is provided. The sol should have a pH such that the particles have a negative surface charge. For example, if the particles are silica, the sol
10 should be alkaline with a pH greater than 7, preferably greater than 8, more preferably greater than 9. It is preferred that the sol include ammonium hydroxide or the like so that NH_4^+ is available as a counter cation for the particles having the negative surface charge.

- A suitable surface treatment agent is then blended into the sol. One
15 preferred class of coupling agents is the silyl(meth)acrylates of which the following silane coupling agent is a representative example:



- 20 This kind of coupling agent reacts with the colloidal particles such that the SiO_x moiety bonds to the particles, while the carbon-carbon double bond remains available for copolymerization with the curable binder component to the extent the curable binder component includes radiation curable materials. Typically, about 10 parts by weight of the surface treatment agent is used per 100 parts by weight of
25 colloidal particles.

After the surface treatment agent is allowed to react with the particles, the curable binder component, such as the free radically curable monomers, is added to the composition. The composition is then heated to remove substantially all of the water. For example, removing about 98% of the water, thus leaving about 2%

water in the composition, has been found to be suitable. When the curable binder component comprises free radically curable prepolymers, the resultant dried composition is a clear liquid. As soon as substantially all of the water is removed, an organic solvent of the type described above is added, if desired, in an amount such that the composition includes from 50% to about 90% by weight solids. After adding the solvent, the antistatic agent and the nonionic surfactant may be added. The preferred antistatic agents and nonionic surfactants described above are very soluble in the composition and dissolve very quickly. After these ingredients are dissolved, catalyst, initiator, color dyes, and any other desired optional additives may be added.

The resultant composition is then coated onto any substrate for which it is desired to improve the abrasion resistance, impact resistance, antistatic properties, combinations of these, or the like while also maintaining optical clarity if desired. Examples of such substrates include any and all thermosetting or thermoplastic items such as camera lenses, eyeglass lenses, binocular lenses, retroreflective sheeting, automobile windows, building windows, train windows, boat windows, aircraft windows, vehicle headlamps and taillights, display cases, eyeglasses, watercraft hulls, road pavement markings, overhead projectors, stereo cabinet doors, stereo covers, furniture, bus station plastic, television screens, computer screens, watch covers, instrument gauge covers, optical and magneto-optical recording disks, and the like.

Any suitable coating technique can be used for applying the composition to the substrate, depending upon the nature of the substrate, the viscosity of the composition, and the like. Examples of suitable coating techniques include spin coating, gravure coating, flow coating, spray coating, coating with a brush or roller, screen printing, knife coating, curtain coating, slide curtain coating, extrusion, squeegee coating, and the like. Typical protective coatings of the present invention have a thickness in the range from about 1 micron to about 100 microns, preferably about 2 to about 50 microns, more preferably about 4 to about 9 microns. Generally, coatings that are too thin may not have sufficient abrasion and/or impact resistance, and films that are too thick may tend to be too heavy depending upon

the nature of the substrate. Also, thicker films, may have more of a tendency to crack.

After coating, the solvent is flashed off with heat. If radiation curable, the coated composition is then cured by irradiation with a suitable form of energy, such as heat energy, visible light, ultraviolet light or electron beam radiation. Irradiating with ultraviolet light in ambient conditions is presently preferred due to the relative low cost and speed of this curing technique. Irradiation causes the radiation curable prepolymers and the functionalized silica particles to crosslink together to form a coating comprising a polymer matrix having the particles, the antistatic agent, the nonionic surfactant, and the optional additives, if any, interspersed in the polymer matrix. The resultant coated substrate is thereby protected against abrasion resistance, impact resistance, and static charge build up.

According to an alternative approach for making a ceramer coating of the present invention in which the polymeric matrix is a partially hydrolyzed organofunctional silane resin, an excess of organofunctional silane monomers is added to an aqueous sol of the type described above. "Excess" means that enough of the silane monomers are added to both surface treat the colloids as well as form the polymeric matrix. Generally, adding 70 parts by weight of silane monomers per 30 parts by weight of colloids would be suitable. The antistatic agent and surfactant are also added, as described above.

Generally, the organofunctional silane monomers will begin to crosslink upon being added to the aqueous sol. If the sol is not going to be used immediately, the shelf life can be extended up to about one month by adding isopropyl alcohol to the composition and then keeping the composition cooled in dry ice. Generally, adding enough isopropyl alcohol such that the resultant composition includes about 50% by weight isopropyl alcohol would be suitable. When ready to be coated, the composition may be coated onto the desired substrate as described above. The coating is then baked to flash off solvent and thermally cure the silane monomers.

The present invention will now be further described with reference to the following Examples. Test procedures used throughout the Examples were as follows:

5

Test Procedure I:**Surface Resistivity Test.**

This test was conducted according to the procedure of ASTM Standard D-257 "D.C. Resistance or Conductance of Insulating Materials". The film samples were cut into 45 x 54 mm samples and conditioned for at least 3 hours at 10 21 \pm 1 %, 30 \pm 1 % and 38 \pm 1 % RH (relative humidity) with the ambient temperature kept constant at 23 \pm 1°C. The surface resistivity (ρ_s) was measured under these conditions using an ETS Model 872 Wide Range Resistance Meter fitted with a Model 803B probe (Electro-Tech Systems, Inc., Glenside, PA). This apparatus applies an external voltage of 100 Volts across two concentric ring 15 electrodes and provides surface resistivity readings in the recommended range from 10^3 to 10^{12} ohm/square with 6×10^{13} ohm/square being the uppermost limit detectable by the apparatus. Within the context of the present invention, samples that display surface resistivities equal or higher than 6×10^{13} ohm/square are considered not antistatic.

20

Test Procedure II:**Determination of Static Charge Dissipation Time (CDT).**

In this test, the static charge dissipation characteristics of coated and uncoated polyester film samples were measured. The films were cut into 45 x 54 25 mm samples and conditioned for at least 3 hours at 21 \pm 1%, 30 \pm 1 % and 38 \pm 1% relative humidity (RH) at T = 23 \pm 1°C. The CDT was measured according to Federal Test Method Standard 101B, Method 4046, "Antistatic Properties of Materials" using an ETS Model 406C Static Decay Test Unit (manufactured by Electro-Tech Systems, Inc., Glenside, PA). This apparatus deposits a charge on the 30 surface of the film by a high voltage (5000 Volt) corona discharge and a fieldmeter

- allows observation of the decay time of the surface voltage from 5000 Volt to 0 Volt. The lower the static discharge times, the better the antistatic properties of the film. All reported values of the CDTs (See Table I) in this invention are averages over at least 4 separate determinations. Values in Table I labeled "infinity" indicate that the material tested is not antistatic, i.e., the tested sample has an initial static charge which cannot be removed by surface conduction. This initial static charge is detected by the fieldmeter of the Static Decay Test Unit as soon as the sample is placed in the test electrodes even in the absence of an external applied voltage.
- 10

Test Procedure III:

Determination of the Optical Clarity.

- The relative optical clarity of all samples in the following examples were determined by measuring their haze according to the procedure of ASTM Standard D-1003-95 "Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics", wherein the method recommended in paragraph X2 "Alternative Haze (Short-cut) Procedure" was followed. In this short-cut procedure the observed haze of a sample (i.e., the percent of transmitted light that is scattered so that its direction deviates more than a specified angle from the direction of the incident beam) was determined at 23°C using a Pacific Instruments Model XL211 Hazemeter (Gardner Neotec Instrument Division, Silver Springs, MD) equipped with an integrating sphere. The lower the percent haze value, the higher the optical clarity of the sample under consideration. Within the context of this invention, samples that display a percent haze equal to or less than 10 are judged to be of acceptable optical clarity.
- 15
- 20
- 25

Example 1:

- This example determines the typical antistatic properties of the bare polyester film used as the coating substrate throughout the examples of this invention.
- 30

5 Sheets of bare polyester film having a thickness of 175 micrometer (obtained from ICI America under the designation 505P) were humidity conditioned and subjected to Test Procedures I and II above. As seen in Table I, the surface resistivity of these samples exceeded 6×10^{13} ohm/square (which is the uppermost limit of the instrument) at all humidity levels; their charge dissipation times were infinite, indicating that the bare (uncoated) sheets of polyester film used throughout the examples of this invention are not antistatic. As shown in Table I, the percent haze of these sheet samples, determined according to Procedure III, was found to be 0.6, indicating excellent optical clarity.

10

Example 2:

This example illustrates the typical chemical preparation, coating and curing of a ceramer hardcoat derived from an alkaline silica sol.

15 In a round-bottomed flask were mixed 1195g Nalco 2327 silica sol (an ammonium ion-stabilized dispersion) having a pH of 9.3 of colloidal silica particles (40% solids) with an average particle diameter of 20 nanometers, available from Nalco Chemical Co., Chicago, IL, 118g N,N-dimethyl acrylamide (Aldrich Chemical Co.), 120g 3-(trimethoxysilyl)propyl methacrylate coupling agent (Aldrich) and 761g Pentaerythritol acrylate (Aldrich). The round-bottomed
20 flask was then mounted on the vacuum line of a Buchi R152 Rotavapor (Buchi Laboratory AG, Flanil, Switzerland) with the bath temperature set at 55°C. A refrigerated mixture of 50% deionized water/50% antifreeze (Texaco) recirculated through the cooling coils. Volatile components were removed at a reduced pressure of 25 Torr until the distillation rate was reduced to less than 5 drops per
25 minute (approximately 2 hours). The resulting material (1464 g) was a clear liquid dispersion of acrylated silica particles in a mixture of N,N dimethyl acrylamide and pentaerythritol acrylate monomers (a ceramer).

4 parts of the above ceramer were added to 21 parts isopropanol and 0.14 parts Irgacure 184 photoinitiator to form a 16% clear, crosslinkable ceramer
30 dispersion in isopropanol. This 16% dispersion was coated onto polyester sheets.

Immediately after coating, the coated sheets were placed in a forced air convection oven for 2.5 minutes at 67°C to flash off the isopropanol. Next, the coated sheets were placed onto the conveyor belt of a UV Curing Station (Model MC-6RQN, Fusion UV Curing Inc., Rockville, MD) equipped with a Fusion "H" lamp. The resulting cured coatings on the polyester sheets were perfectly clear to the eye. The average percent haze of the coated sheets, measured according to Test Procedure III was 0.7%.

Samples of the cured coating were conditioned to 21%, 30% and 38% relative humidity and their surface resistivity measured according to Test Procedures I and II. It is seen from Table I that the surface resistivities for this example exceeded 6×10^{13} ohm/square at all three humidity levels, while the charge dissipation times were infinite in all cases, indicating that the cured ceramer coating is not antistatic.

15

Example 3:

This example illustrates the effect of adding both a siloxane-terminated polyalkylene oxide, nonionic surfactant and a perfluorinated lithium salt LiSO_3CF_3 , upon the antistatic properties of the cured ceramer of Example 2.

To 22.5 g of the 16% ceramer dispersion of Example 2 were added with vigorous agitation 0.6 g of a 16% solution of lithium trifluoromethanesulfonate LiSO_3CF_3 (Aldrich) in isopropanol and 0.3 g of a 16% solution of DOW CORNING 57 surfactant in isopropanol (DOW CORNING 57 is a surfactant additive mixture containing polyethylene glycol diacetate, polyethylene glycol monoallyl ether acetate, and dimethyl, methyl(polyethylene oxide acetate-capped) siloxane). The resulting dispersion was somewhat hazy, but the addition of 1.0 g deionized water rendered the dispersion crystal clear. The clarified dispersion was coated and cured on polyester sheets in exactly the same fashion as in Example 2. The average percent haze of the coated sheets was 1.4%. As seen in Table I, the observed charge decay times of the coating after the required humidity conditioning dramatically dropped to 1.54 seconds at 21% R.H, 0.8 seconds at 30%

R.H. and 0.6 seconds at 38% R.H. Similarly, the observed surface resistivities significantly dropped to 4×10^{11} ohm/square at 21% R.H., 1.9×10^{11} ohm/square at 30% R.H. and 6×10^{10} ohm/square at 38% R.H.

5

Example 4:

This example illustrates the effect of adding both a perfluoro-terminated polyalkylene oxide surfactant and perfluorinated lithium salt LiSO_3CF_3 on the antistatic properties of the cured ceramer of Example 2.

To 22.5 g of the 16% ceramer dispersion of Example 2 were added with
10 vigorous agitation 0.6 g of a 16% solution of lithium trifluoromethanesulfonate (LiSO_3CF_3) and 0.6 g of a 16% solution of ZONYL FSN fluorosurfactant in isopropanol (ZONYL FSN is a fluorocarbon-terminated polyethylene oxide surfactant available from Aldrich Chemical Co., Milwaukee, Wisconsin). The resulting dispersion was somewhat hazy, but the addition of 0.5 g deionized water
15 rendered the dispersion crystal clear. The clarified dispersion was coated and cured on polyester sheets in exactly the same fashion as in Example 2. The average percent haze of the coated sheets was 1.3%. As seen in Table I, the observed charge decay times of the coating after the required humidity conditioning dramatically dropped to 2.3 seconds at 21% R.H., 0.9 seconds at 30%
20 R.H. and 0.6 seconds at 38% R.H. Similarly, the observed surface resistivities significantly dropped to 7×10^{11} ohm/square at 21% R.H., 2.0×10^{11} ohm/square at 30% R.H. and 2×10^{10} ohm/square at 38% R.H.

Example 5:

25

This example illustrates the effect of adding both a perfluoro-terminated polyalkylene oxide surfactant and perfluorinated lithium salt $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ on the antistatic properties of the cured ceramer of Example 2.

To 45 g of the 16% ceramer dispersion of Example 2 were added with
vigorous agitation 2.5 g of a 16% solution of lithium
30 di(trifluoromethanesulfone)imide ($\text{LiN}(\text{SO}_2\text{CF}_3)_2$) and 2.5 g of a 16% solution of

ZONYL FSN fluorosurfactant in isopropanol. The resulting dispersion was somewhat hazy, but the addition of 1.0 g deionized water rendered the dispersion crystal clear. The clarified dispersion was coated and cured on polyester sheets in exactly the same fashion as in Example 2. The average percent haze of the coated sheets was 1.3%. The coated sheets were conditioned for at least 3 hours at 30% R.H. and their charge Dissipation time and surface resistivity measured as in Test Procedures I and II. As seen in Table I, the average charge decay time of the coating dramatically dropped to 0.36 seconds at 30% R.H., while the surface resistivity significantly dropped to 3×10^{11} ohm/square.

10

Example 6:

This example illustrates the antistatic properties of a ceramer composition containing about half the amount of acrylated silica relative to the composition in Example 3.

15 In a first step, a mixture consisting of 10 parts by weight N,N-dimethyl acrylamide (NNDMA), 37 parts pentaerythritol triacrylate and 2 parts Irgacure 184 was prepared. 4 g of this mixture were added to 21g isopropanol to result in a 16% crosslinkable solution (compound A). In a second step, 22.5 g of this 16% solution were added to 0.3 g of a 16% solution of DOW CORNING 57 surfactant in
20 isopropanol and 0.7 g of a 16% solution of FC-122 in isopropanol (compound B). In a third step, 11.25 g of compound B were added to 11.25 g of the 16% ceramer dispersion prepared in Example 3. Note that the resulting 16% ceramer dispersion (compound C) contains about half the relative amount of acrylated silica than the 16% ceramer dispersion prepared in Example 3.

25 Compound C was coated and cured on polyester sheets in exactly the same fashion as in Example 2. The average percent haze of the coated sheets was 0.9%. As seen in Table I, the observed charge decay times of the coating after the required humidity conditioning dramatically dropped to 4.24 seconds at 21% R.H., 2.55 seconds at 30% R.H. and 1.6 seconds at 38% R.H. Similarly, the observed
30 surface resistivities significantly dropped to 4×10^{11} ohm/square at 21% R.H.,

7 x 10¹¹ ohm/square at 30% R.H. and 3 x 10¹¹ ohm/square at 38% R.H.

Example 7:

This example illustrates the antistatic properties of a ceramer composition
5 containing about one third the relative amount of acrylated silica than that in
Example 3.

To 9.2 parts of compound B from Example 5 were added 5.6 parts of the
16% ceramer dispersion of Example 3. Note that the resulting 16% ceramer
dispersion (compound D) contains about one third the relative amount of acrylated
10 silica in the 16% ceramer dispersion prepared in Example 3.

Compound D was coated and cured on polyester sheets in exactly the same
fashion as in Example 2. The average percent haze of the coated polyester sheets
was 0.9%. As seen in Table I, the observed charge decay times of the coating after
the required humidity conditioning dramatically dropped to 4.62 seconds at 21%
15 R.H., 2.90 seconds at 30% R.H. and 1.9 seconds at 38% R.H. Similarly, the
observed surface resistivities significantly dropped to 2 x 10¹² ohm/square at 21%
R.H., 7 x 10¹¹ ohm/square at 30% R.H. and 5 x 10¹¹ ohm/square at 38% R.H.

Example 8:

20 This example illustrates the effect of adding a polyalkylene oxide surfactant
alone on the antistaticity of the cured ceramer of Example 2.

To 22.5 g of the 16% ceramer dispersion of Example 2 were added with
vigorous agitation 0.6 g of a 16% solution of ZONYL FSN fluorosurfactant in
isopropanol. The resulting clear dispersion was coated and cured on polyester
25 sheets in exactly the same fashion as in Example 2. The average percent haze of
the coated sheets was 1.2. As seen in Table I the observed surface resistivity of
this coating was still very high at 6 x 10¹³ ohm/square while the static decay time
values remained infinite at all three conditioning humidity levels considered in this
study, indicating that when the said surfactant is added alone to the ceramer

composition, it has no observable effect on the static properties of the ceramer within the relative humidity range considered in this study.

Example 9:

5 This example illustrates the effect of added perfluorinated lithium salt LiSO_3CF_3 alone on the antistatic properties of the cured ceramer of Example 2.

To 22.5 g of the 16% ceramer dispersion of Example 2 were added with vigorous agitation 0.6 g of a 16% solution of lithium trifluoromethanesulfonate in isopropanol. The resulting clear dispersion was coated, cured and humidity
10 conditioned on polyester sheets in exactly the same fashion as in Example 2. The average percent haze of the coated polyester sheets was 1.0%. As seen in Table I the observed surface resistivity of this cured composition was still in excess of 6×10^{13} ohm/square while the static decay times remained infinite, indicating that the added perfluorinated lithium salt alone has a negligible effect on the static
15 properties of the ceramer of Example 2.

Example 10:

This example illustrates the typical chemical preparation, coating and curing of a second ceramer hardcoat derived from an alkaline silica sol.

20 In a round-bottom glass flask I mixed with vigorous agitation 119 g Nalco 2327 silica sol, 12 g 3-(trimethoxysilyl)propyl methacrylate coupling agent (DOW CORNING Z6030), 48 g 2-hydroxyethyl acrylate (Aldrich) and 48 g pentaerythritol triacrylate (Aldrich). Water was extracted using a Buchi 121 Rotavapor (Buchi Laboratory AG, Flanil, Switzerland) at a vacuum pressure of
25 about 90 Torr and with the water-bath temperature set at 55°C. The resulting anhydrous dispersion was crystal clear and almost water-thin. Next, 4 g of this anhydrous dispersion were added to 21g isopropyl alcohol and 0.16 g Irgacure 184 photoinitiator to give a 16% dispersion in the solvent. This 16% dispersion was coated on polyester sheets and subsequently cured in exactly the same fashion as in

Example 2. The resulting cured coating on the polyester sheets was perfectly clear to the naked eye. The observed average percent haze of the coated sheets was 1.2.

Samples of the cured coating were conditioned to 21%, 30% and 38% relative humidity and their surface resistivity measured according to Test Procedures I and II. It is seen from Table I that the surface resistivities for this example were higher than 6×10^{12} ohm/square at all three humidity levels, while the charge dissipation times were in all cases infinite, indicating that the cured ceramer coating is not antistatic.

10

Example 11:

This example illustrates the effect of adding both a polyalkylene oxide surfactant and perfluorinated lithium salt LiSO_3CF_3 on the antistatic properties of the cured ceramer of Example 10.

To 22.5 g of the 16% ceramer dispersion of Example 10 were added with vigorous agitation 0.6 g of a 16% solution of lithium trifluoromethanesulfonate (LiSO_3CF_3) and 0.3 g of a 16% solution of DOW CORNING 57 surfactant additive. The resulting dispersion was crystal clear and was coated and cured on polyester sheets in exactly the same fashion as in Example 2. The average percent haze of the coated construction was 1.4. As seen in Table I, the observed charge decay times of the coating after the required humidity conditioning dramatically dropped to 1.6 seconds at 21% R.H., 0.6 seconds at 30% R.H. and 0.5 seconds at 38% R.H. Similarly, the observed surface resistivities significantly dropped to 4×10^{11} ohm/square at 21% R.H., 7.3×10^{10} ohm/square at 30% R.H. and 5×10^{10} ohm/square at 38% R.H.

20

Example 12:

This example illustrates the antistatic properties of a ceramer derived from an acidic silica sol and having the same organic phase as Example 10.

In a glass round-bottom flask I mixed 67.15 g NALCO1042 silica sol (an acidic silica sol (34% solids) having a pH = 2.8 and average particle diameter of 20

nanometers, available from Nalco Chemical Co., Chicago, IL), 11.2 g 2-hydroxyethyl acrylate, 5.6 g 3-(trimethoxysilyl)propyl methacrylate coupling agent, and 7.9g pentaerythritol. Water was extracted using a Buchi 121 Rotavapor exactly as in Example 10. The resulting anhydrous dispersion was crystal clear and almost water-thin. Next, 4 g of this anhydrous dispersion were added to 21 g isopropyl alcohol and 0.14 g Irgacure 184 photoinitiator to give a 16% dispersion in the solvent. This 16% dispersion was coated on polyester sheets and subsequently cured in exactly the same fashion as in Example 2. The resulting cured coating on the polyester sheets was optically clear to the naked eye. The average percent haze of the coated sheets was 1.2.

Samples of the cured coating were conditioned to 21%, 30% and 38% relative humidity and their surface resistivity measured according to Test Procedures I and II. It is seen from Table I that the surface resistivities for this example were higher than 6×10^{13} ohm/square at all three humidity levels, while the charge dissipation times were infinite, indicating that the cured ceramer coating is not antistatic.

Example 13:

This example illustrates the effect of adding both a polyalkylene oxide surfactant and perfluorinated lithium salt LiSO_3CF_3 on the antistatic properties of the cured ceramer of Example 12.

To 22.5 g of the 16% ceramer dispersion of Example 12 were added with vigorous agitation 0.6 g of a 16% solution of lithium trifluoromethanesulfonate (LiSO_3CF_3) and 0.3 g of a 16% solution of DOW CORNING 57 surfactant additive. The resulting dispersion was somewhat hazy, but the addition of 1 g deionized water rendered the dispersion crystal clear. This crystal clear dispersion was coated and cured on polyester sheets in exactly the same fashion as in Example 2. The average percent haze value of the coated sheets was 1.5.

Samples of the cured coating were conditioned to 21%, 30% and 38% relative humidity and their surface resistivity measured according to Test